Low-Energy Solvents for CO_2 Capture Enabled by a Combination of Enzymes and Vacuum Regeneration

Alan House

novozymes
Rethink Tomorrow

DOOSAN

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

UK UNIVERSITY OF KENTUCKY
Center for
Applied Energy Research

AIChE 2014 meeting
Atlanta, GA
November 17, 2014

Notices

- **ACKNOWLEDGEMENT OF GOVERNMENT SUPPORT.** This material is based upon work supported by the Department of Energy under Award Number DE-FE0007741.
-
-

Agenda

- Project Overview
    - Carbonic anhydrase for CO_2 capture
    - Partners, budget & objective
- Technology Background
    - Process concept
    - Fundamental mechanism
- Progress and Status
    - Bench-scale system description
    - Parametric test results
    - 500-h run initial test results
- Conclusions & Next Steps

novozymes Rethink Tomorrow

Carbonic anhydrase for CO_2 capture: a select survey of other public projects

- Codexis
  - DE-AR0000071
  - PE dissolved CA for 4.2 M MDEA and >85°C
  - Stable performance, 60 h test at NCCC
- Akermin
  - DE-FE0004228
  - Immobilize CA in absorber
  - Stable performance, 116 days at NCCC
- Illinois State Geological Survey, Prairie Research Institute, Yongqi Lu Laboratory
  - DE-FC26-08NT0005498 and others
  - Evaluate process concepts, immobilization options, temp. stability, kinetics, etc.

About the NCCC:

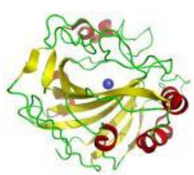
- The National Carbon Capture Center provides a slipstream from a 880 MW coal unit for testing post-combustion CO_2 capture technologies.

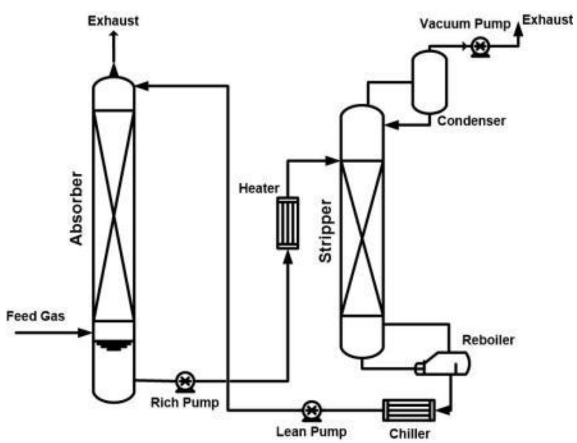
novozymes
Rethink Tomorrow

Project Objective

Complete a *bench-scale study* and corresponding full technology assessment to validate the potential in meeting the DOE Program Objectives of a *solvent-based post-combustion carbon dioxide capture* system that integrates

$CO_2 + H_2O + K_2CO_3 \leftrightarrow 2KHCO_3$





- a **low-enthalpy**, aqueous potassium carbonate-based solvent
- with an **absorption**-enhancing (*dissolved*) carbonic anhydrase enzyme catalyst
- and a low temperature vacuum **regenerator**
- in a **re-circulating** absorption-desorption process configuration

Novozymes in Brief – World Leader in Bioinnovation
Producing large volume enzymes for industrial applications

1. Improving the production host
Improving the microorganisms' ability to produce more enzymes per m^3 fermentation tank through genetic engineering

2. Optimizing industrial production
- Process optimization
- Equipment optimization
- Input optimization

3. Improving the enzyme produced
Improving the efficacy of the enzymes through protein engineering to meet application conditions and process economy requirements

Project Overview

- Project Participants

Pacific Northwest National Laboratory	Doosan	Novozymes	University of Kentucky Center for Applied Energy Research
Ultrasonics & Aspen®	Full Process Analysis	Enzymes & Solvents	Kinetics & Bench-scale Tests

- DOE Project Manager: Andrew Jones
- Project Number: DE-FE0007741
- Total Project Budget: $2,088,644
  - DOE: $1,658,620
  - Cost Share: $430,024
- Project Duration: Oct. 1, 2011 – March 31, 2015

DOE Program Objectives
Develop solvent-based, post-combustion technology that
- Can achieve ≥ 90% CO_2 removal from coal-fired power plants
- Demonstrates progress toward the DOE target of <35% increase in LCOE.

Process Concept, Advantages & Challenges

Stable, benign, non-volatile aq. K_2CO_3-based **solvent** does not require water wash

Enzyme-enhanced CO_2 mass transfer **reduces absorber size** to feasible height

Dissolved enzyme enables liquid dosing

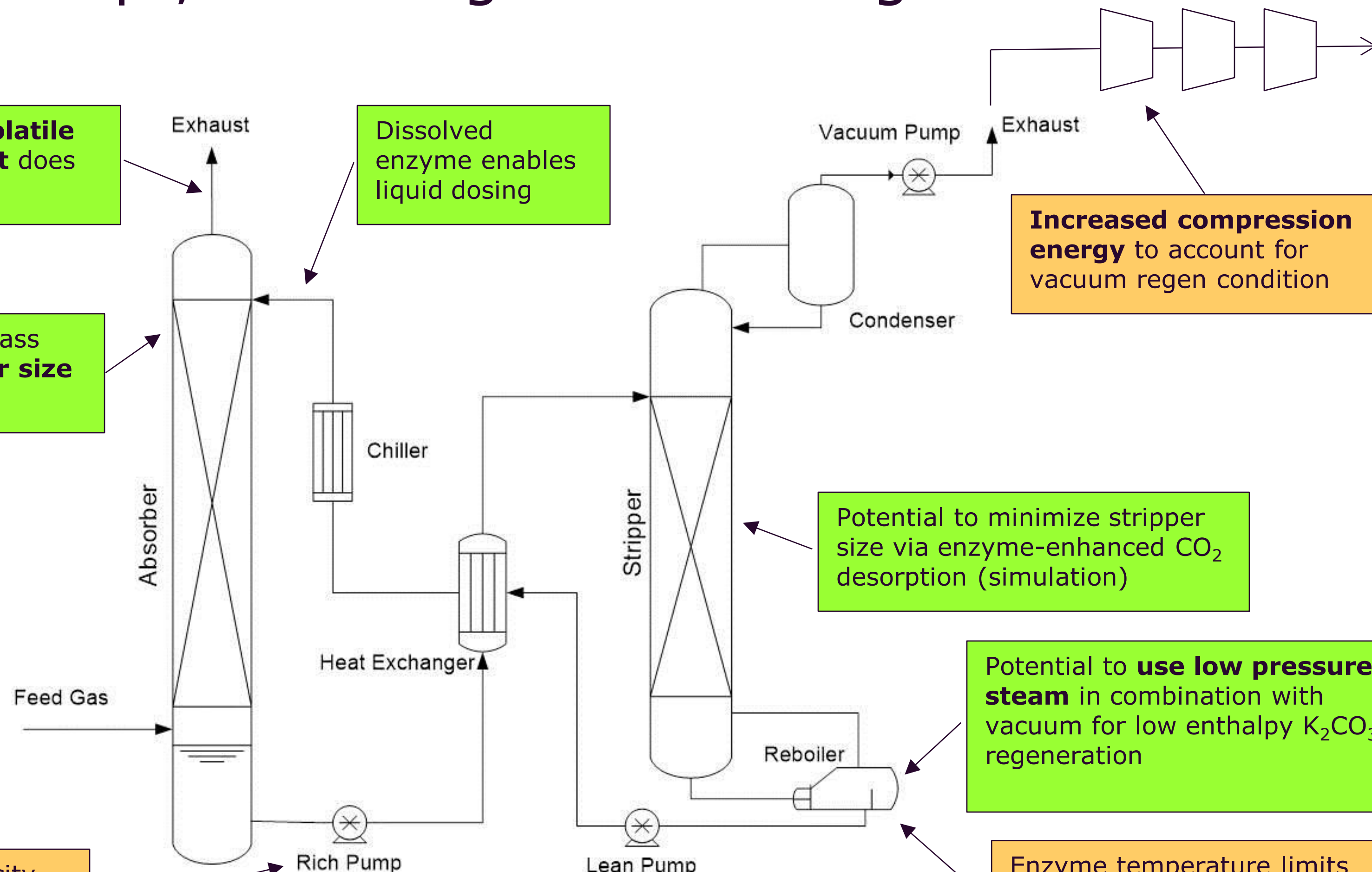
Increased compression energy to account for vacuum regen condition

Potential to minimize stripper size via enzyme-enhanced CO_2 desorption (simulation)

Potential to **use low pressure steam** in combination with vacuum for low enthalpy K_2CO_3 regeneration

K_2CO_3 loading capacity limit may increase solvent circulation rate

Enzyme temperature limits may result in **high enzyme replenishment** requirement



Absorption
1 atm/30-40°C

Regeneration
~0.35 atm/76°C

Generating Bench-scale Test Data

novozymes
Rethink Tomorrow

Enzyme Enhanced CO_2 Absorption Mechanism

Gas Side | Gas-Liquid Interface | Liquid Side (pH>9)

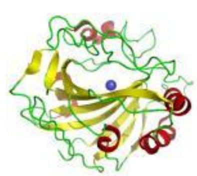
$$CO_{2(aq)} + HO^{-} \leftrightarrow HCO_3^{-}$$

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$

$KHCO_3$-

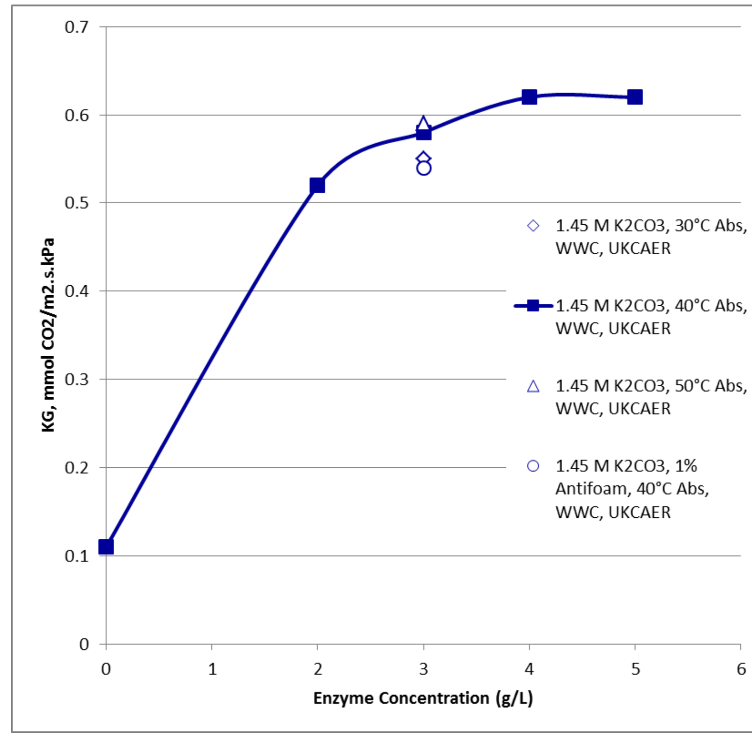
K_2CO_3

$$CO_{2(aq)} + 2H_2O \leftrightarrow HCO_3^{-} + H_3O^{+}$$



$KHCO_3$-

Enzyme adds value because, without catalyst, liquid side reaction kinetics are overall mass transfer rate limiting



Overall Mass Transfer Coefficient (K_g) Enhanced by Enzyme in WWC

novozymes
Rethink Tomorrow

Bench-scale Unit Description

- Flow Rates
  - Gas: 30 SLPM (15% CO_2)
  - Liquid : 300-600 ml/min
- Liquid Temperature
  - Absorber Inlet: 30-40°C
  - Stripper Inlet: ~65°C
  - Reboiler Oil Inlet: 90-95°C
- Stripper Pressure: 0.35 atm absolute
- K_2CO_3 Concentration: 23 wt%
- Enzyme Concentration: 0 – 4 g/L

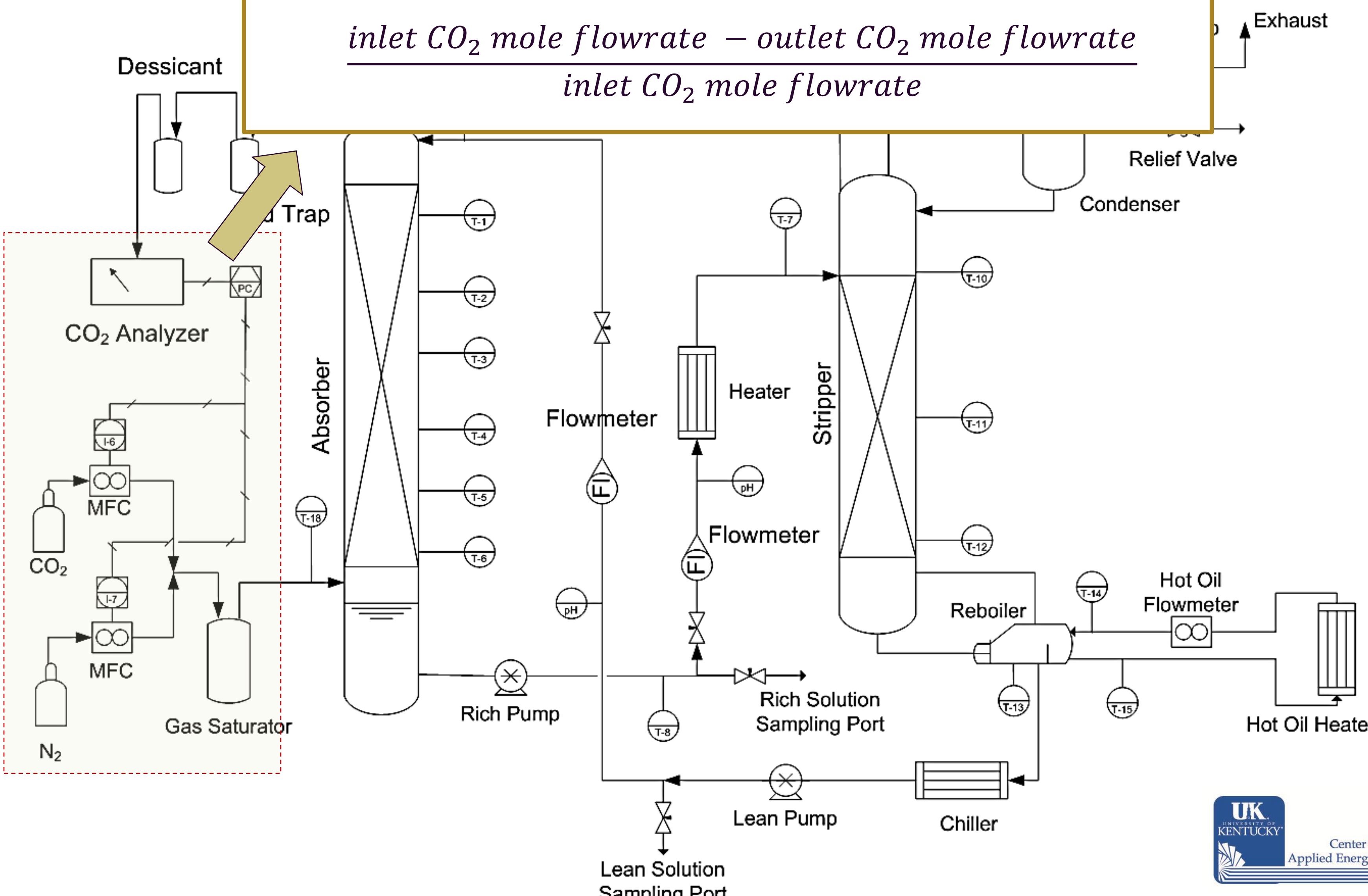
UK University of Kentucky
Center for Applied Energy Research

PFD of Integrated Bench-scale System

novozymes
Rethink Tomorrow

Capture Efficiency=

$$\frac{inlet\ CO_2\ mole\ flowrate\ \ -outlet\ CO_2\ mole\ flowrate}{inlet\ CO_2\ mole\ flowrate}$$

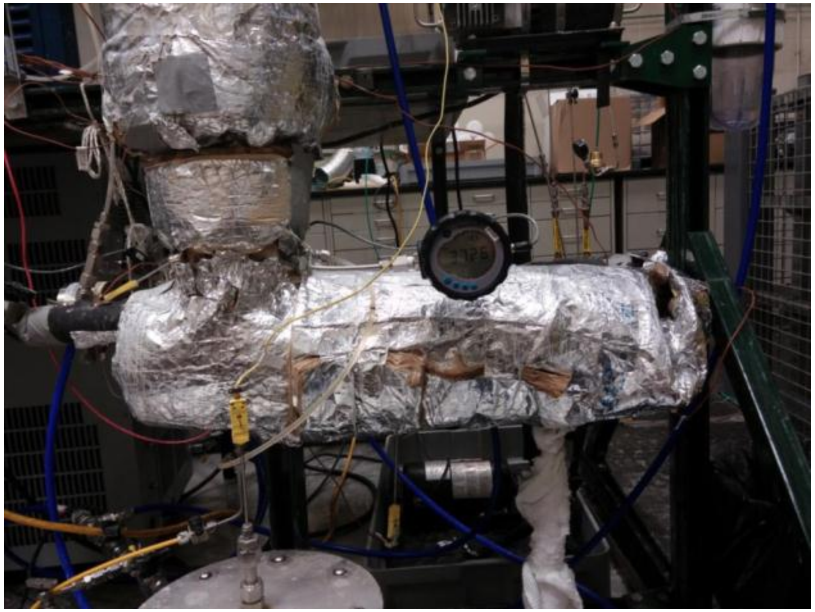


UK University of Kentucky
Center for Applied Energy Research

Bench-scale Operational Observations

Absorber bottom

Stripper top



Stripper bottom

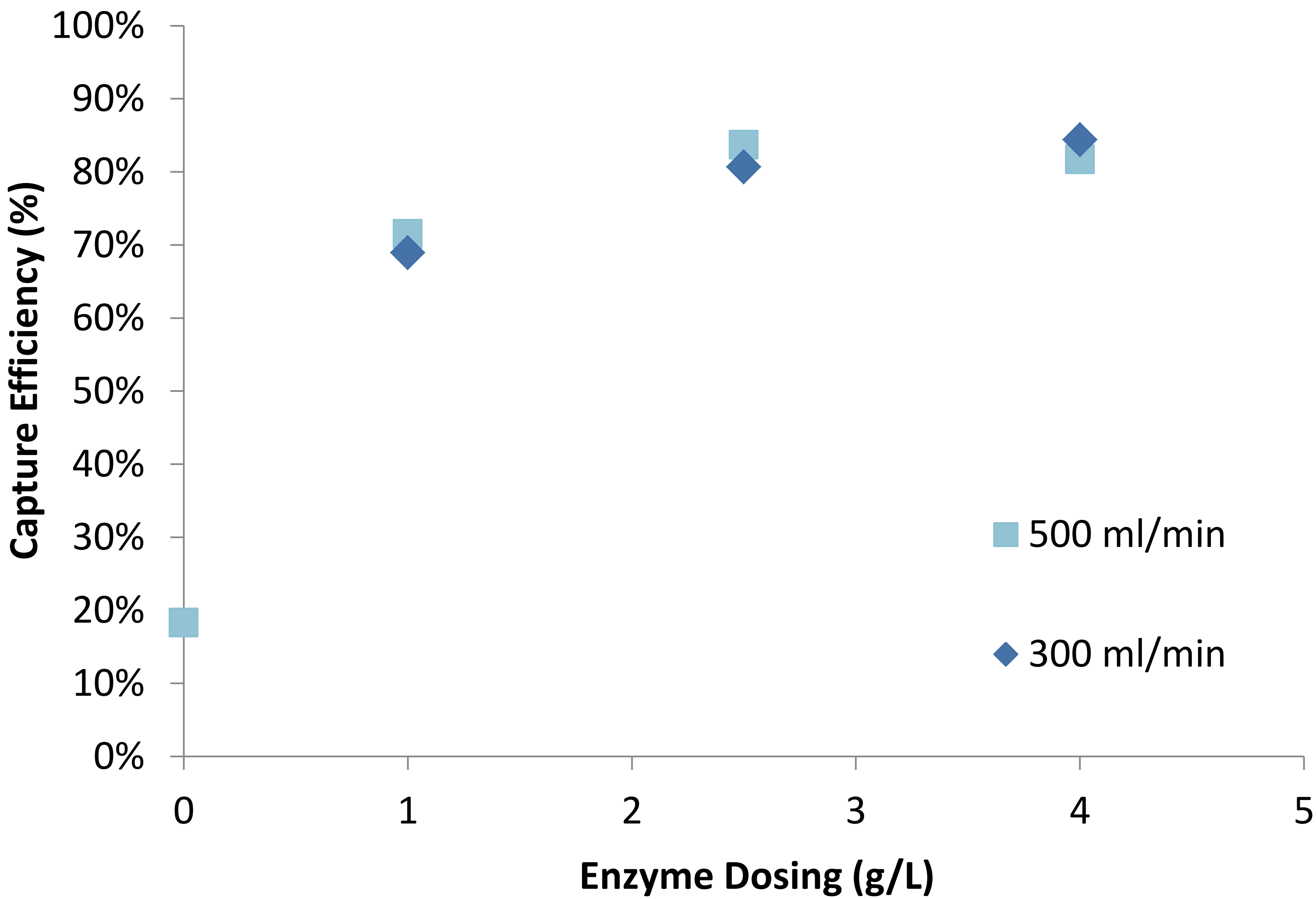
Absorber

- Low temp difference along absorber length due to low enthalpy solvent
- No visual change in packing
- Rich solvent filter removes solids

Stripper

- Water cooled condenser at top
- Tube and shell reboiler
- Antifoam dosing effectively mitigates foaming
- Bulk temp. ranges from 65°C (rich solvent inlet to stripper top) to 76°C (reboiler)
- Reboiler heating source temp. 90-95°C
- Lean solvent filter removes solids

Impact of Enzyme Conc. and Liquid Flow Rate

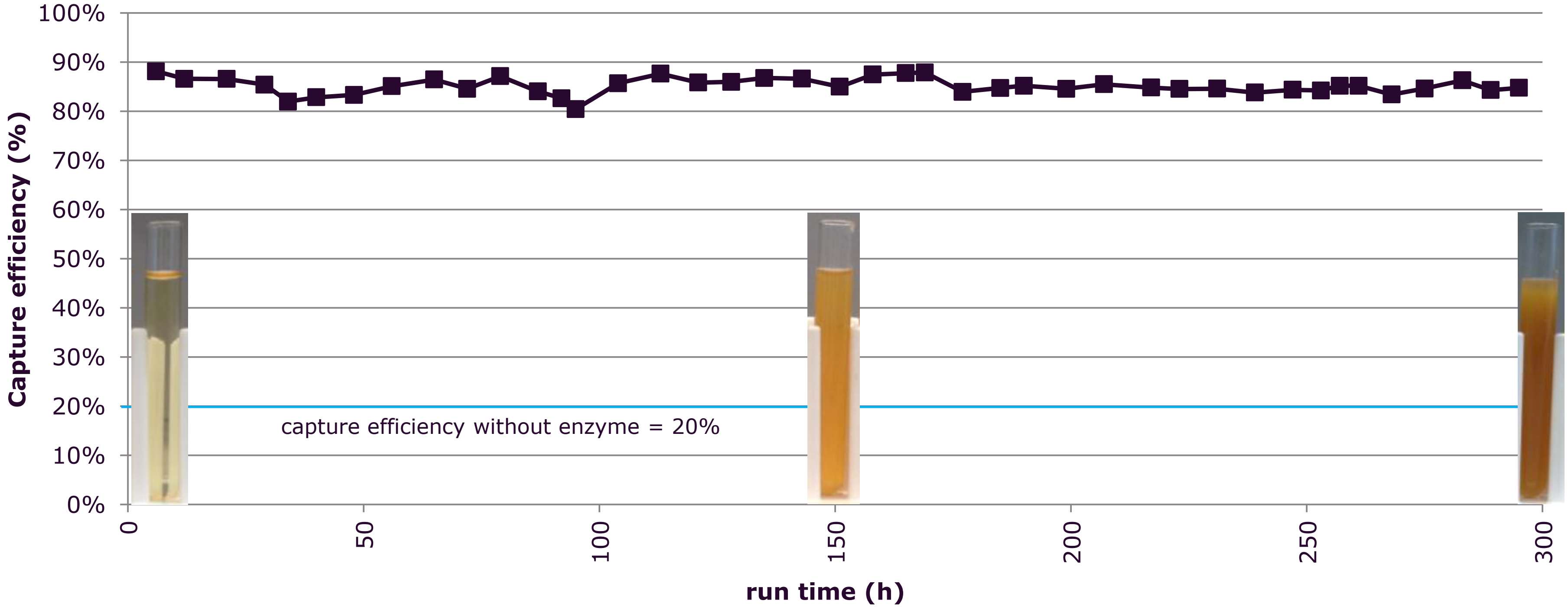


500 Hour Long Term Test

- Baseline conditions
  - 40°C absorber
  - 95°C reboiler heating source temperature
  - 0.35 atm absolute stripper top pressure
  - 500 ml/min liquid flow rate
  - 30 SLPM gas flow rate; 15% CO_2
  - 2.5 g/L active enzyme dose
  - 23 wt% K_2CO_3
- Solvent additions per ~7 h run day
  - Antifoam addition: ~0.04%
  - Active enzyme addition: ~20% of active enzyme dose
    - Defining enzyme replenishment is part of the program
    - Active enzyme replenishment is at least 7% of total enzyme
  - Solvent volume and alkalinity are maintained

novozymes Rethink Tomorrow

500 Hour Long Term Test Results

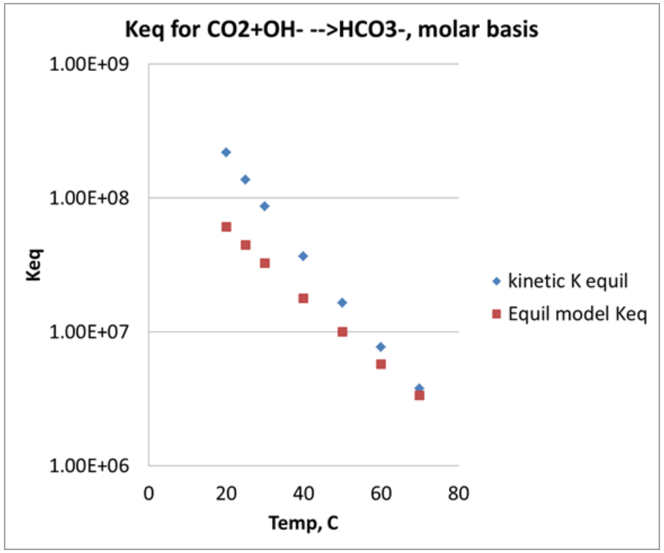


- >80% CO_2 Capture efficiency maintained
- Solvent darkens and becomes turbid
- Principle of using dissolved enzyme replenishment to achieve stable operation demonstrated

Approach to Kinetic Model

- Improve existing ASPEN kinetic model for $CO_2+OH^- \rightarrow HCO_3^-$
  - Include data representing a wider temperature range than prior model
  - Include the effects of ionic strength on rate
  - Correct existing reverse kinetics to provide agreement with equilibrium model predictions at temperatures <70°C.
- Include a parallel rate expression for $CO_2+2H_2O \rightarrow H_3O^+ + HCO_3^-$
  - Model enzyme effect by accelerating this reaction, not hydroxide reaction

Comparison of equilibrium constants predicted by equilibrium model and pre-correction kinetic model.



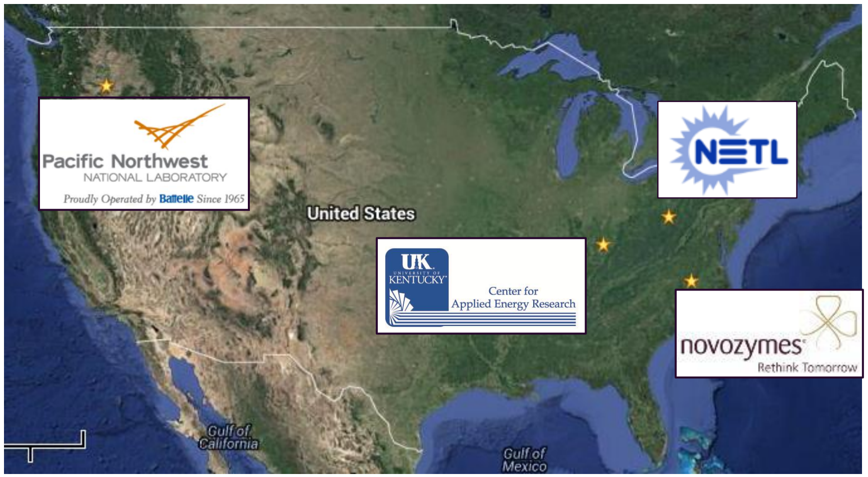
Conclusions and Next Steps

- Conclusions
  - 30 SLPM benchscale unit is operational and providing unique test data for low P/low T stripping with enzyme-enhanced K_2CO_3-based solvent
  - Parametric testing resulted in selection of 500 hour test conditions operating at >80% capture
  - Current enzyme longevity is significantly diminished by travel through stripper, but can be mitigated for test purposes by replenishment program
- Next Steps
  - Complete 500 hour testing
  - Prepare full TEA, with updated kinetics-based process simulation and ASPEN models
  - Complete EH&S assessment
- Potential Future Developments
  - Improve enzyme thermal stability
    - Immobilization or chemical modification to create physical barrier to unfolding
    - ID alternate enzyme candidates and/or protein engineering to improve T stability
    - Explore alternate process configurations to reduce enzyme loss
  - Evaluate options for increasing liquid loading capacity

Thank-you

14 AIChE Annual Meeting, Atlanta, GA

novozymes Rethink Tomorrow



Acknowledgements

DOE-NETL
Andrew Jones

Pacific Northwest National Laboratory
Charles Freeman (PM/TL), Mark Bearden
Greg Whyatt

UK-Center for Applied Energy Research
Kunlei Liu (PM), Kun Liu (TL), Guojie Qi
Reynolds Frimpong

Doosan Power Systems
David Fitzgerald (PM), Jonathan Slater (TL)
Rafael Vidal, Tania Russell

Novozymes
Sonja Salmon (PI/PM), Alan House (TL)
Erin Yarborough